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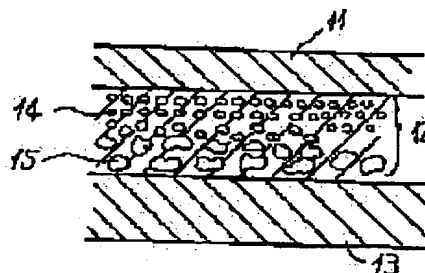
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## (54) ELECTRODE FOR POLYMER SOLID ELECTROLYTE TYPE FUEL CELL

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To improve gas permeability and conductivity of protons and electrons by making the performance of a catalyst layer differing in the thickness direction.

**SOLUTION:** In the case the preciseness of a catalyst carrier, as the performance of a catalyst layer, is made different in the direction of the thickness of the catalyst layer, the following function is provided. An ion exchange membrane 11 side of the catalyst layer 12 is made of a precise carrier 14 and a gas diffusion layer 13 side is made of a porous carrier 15. A fuel gas, e.g. hydrogen and oxygen, is supplied from the lower side of the gas diffusion layer 13 and since the layer is porous, the gas can easily pass through the layer and reaches the interface of both catalyst carriers 14, 15. Since the region from the interface to the carrier 14 is precise, the gas permeability is lowered but the distance through which the gas should pass is made to be a half, the gas permeability as a whole is improved. Meanwhile, protons and electrons produced permeability from the exchange membrane 11 are led to outside through the conductive single body 14 and since the carrier 14 is precise, protons and electrons easily reach the interface of both carriers 14, 15 and the conductivity as a whole is also improved as same as the gas permeability.



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(54) **ELECTRODE FOR POLYMER SOLID**  
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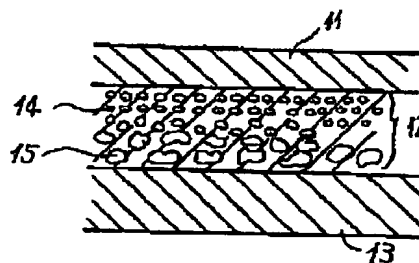
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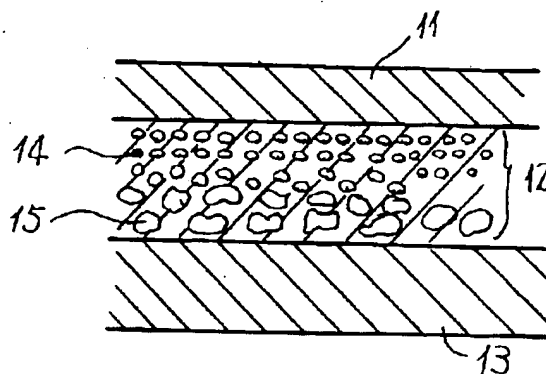
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(54) 【発明の名称】 高分子固体電解質型燃料電池用電極

(57) 【要約】

【目的】 従来の燃料電池では、ガス透過性とプロトン等の導伝性という相反する性能を高レベルで有しえないため、満足できる高性能の燃料電池は存在しない。本発明は、従来の燃料電池用触媒層より高性能の触媒層を有する燃料電池用電極を提供することを目的とする。

【構成】 触媒層12をイオン交換膜11とガス拡散層13で挟んで成る燃料電池の前記触媒層をイオン交換膜側の緻密な触媒担体14とガス拡散層側の多孔質の触媒担体15で構成する等して、触媒層の性能を該触媒層の厚さ方向に異ならせる。



## 【特許請求の範囲】

【請求項1】 触媒が担持された触媒担体とイオン交換樹脂、又は触媒が担持された触媒担体とイオン交換樹脂と親水性樹脂とを含む触媒層が、イオン交換膜とガス拡散層間に形成された高分子固体電解質型燃料電池用電極において、前記触媒層の性能を該触媒層の厚さ方向に異ならせたことを特徴とする高分子固体電解質型燃料電池用電極。

【請求項2】 前記性能がイオン交換樹脂濃度であり、触媒層のイオン交換膜側に高濃度のイオン交換樹脂を使用し、ガス拡散層側に低濃度のイオン交換樹脂を使用する請求項1記載の高分子固体電解質型燃料電池用電極。

【請求項3】 前記性能が触媒担体の比表面積であり、触媒層のイオン交換膜側に比表面積の小さい触媒担体を使用し、ガス拡散層側に比表面積の大きな触媒担体を使用する請求項1記載の高分子固体電解質型燃料電池用電極。

【請求項4】 前記性能が触媒担体の緻密性であり、イオン交換膜側に緻密な触媒担体を使用し、ガス拡散層側に多孔質の触媒担体を使用する請求項1記載の高分子固体電解質型燃料電池用電極。

【請求項5】 前記性能が触媒量であり、イオン交換膜側の触媒量を多くし、ガス拡散層側の触媒量を小さくした請求項1記載の高分子固体電解質型燃料電池用電極。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、高分子固体電解質型燃料電池用電極に関し、より詳細には触媒層とガス拡散層から成る燃料電池用電極における前記触媒層の性能を向上させた前記燃料電池用電極に関する。

## 【0002】

【従来技術及び問題点】燃料電池は、水素や各種化石燃料を用いる高効率、無公害発電装置であることから、エネルギー問題、全地球的公害問題に対処できる、“ポスト原子力”の発電装置として、社会的に大きな期待が寄せられている。火力代替発電用、ビルディングや工場単位のオンサイト発電用、あるいは宇宙用など、用途に応じた各種燃料電池が開発されている。近年、炭酸ガスを中心とする温室効果や、NO<sub>x</sub>、SO<sub>x</sub>等による酸性雨が地球の将来を脅かす深刻な公害として認識されてきた。これら公害ガスの主要な排出源の一つが自動車等の内燃機関であることから、燃料電池を車載用内燃機関に代えて作動するモータ電源として利用する気運が急速に高まりつつある。この場合、多くの付帯設備と同様、電池は可能な限り小型であることが望ましく、そのためには電池本体の出力密度、出力電流密度が高いことが必須である。この条件を満たす有力な燃料電池の候補として、イオン交換膜を用いた高分子固体電解質型燃料電池（以下PEMFCという）が注目されている。

【0003】ここでPEMFCの本体の基本構造と作

用、問題点について説明する。図1に示す如く、PEM1の両側に4A、4Cで示されるアノード及びカソードがホットプレスにより接合されることにより電池の基本が構成される。このアノード及びカソードは2A又は2Cで示される多孔質触媒層と3A又は3Cで示されるカーボンペーパーなどガス拡散層からなる。電極反応は2A及び2C部の触媒表面で起こる。アノード反応ガス（H<sub>2</sub>）は反応ガス供給孔5Aから3Aを通して供給され、カソード反応ガス（O<sub>2</sub>）は反応ガス供給孔5Cから3Cを通して供給される。2A中では、アノード反応： $H_2 \rightarrow 2H^+ + 2e^-$ が、2C中ではカソード反応： $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$ の反応が起こり、電池全体ではこれらの反応のトータルとして $H_2 + 1/2O_2 \rightarrow H_2O + Q$ （反応熱）が起こる。この過程で起電力が得られ、この電気エネルギーにより外部負荷8を電子が流れる際に電氣的仕事が行なわれる。

【0004】燃料電池の反応は前記触媒上で起こり、どのようにして前記触媒を有効利用するか、換言すると触媒層の性能ひいては燃料電池の性能を向上させるかが、前記燃料電池により得られるエネルギー量を左右する最大の要因である。しかしながら従来の燃料電池では種々の理由により触媒層の性能を最大にすることができず、高価な触媒特に白金族金属触媒を有効利用できていないという欠点がある。本発明者らはこの燃料電池の性能を最大にすることができない理由を熟慮した結果、その理由の1つが触媒層が均一であるためであることを見出した。従来から高分子固体電解質型燃料電池用電極の触媒層は、触媒とイオン交換樹脂、又は触媒とイオン交換樹脂と親水性樹脂を、有機溶媒と水との混合液に懸濁した懸濁液を、電極基板上に一度に塗布し、乾燥し、焼成を行なって製造されている。この方法では一度に塗布を行なうため、触媒層の厚み方向で、触媒層の混成原料を変えることができず、触媒層の厚み方向でそれぞれに応じた最適な触媒層を得ることができない。触媒層の主要な機能はアノード及びカソードで生ずるプロトン及び電子を導伝して燃料電池反応を促進する点にある。一方触媒層は反応ガスを供給し、生成ガスを排出するという機能も有し、同じ触媒層でも反応サイトから離れるほど反応を促進しプロトンを導伝する機能よりもガス流通を円滑にする機能の方が重視されるようになる。しかし従来の触媒層は前述の通り均一でありそのガス流通の円滑性を与える触媒担体の緻密性も均一である。

【0005】このガス流通を円滑にする機能つまりガス透過性とプロトン（電子）導伝性とは二律背反的關係にあり、一方を高めると他方が低くなり、従来技術では両者を高めることは不可能である。従来の燃料電池は、前述した通り製造した電極（アノード及びカソード）2枚でイオン交換膜を挟み、これらをホットプレスで結着して製造されている。この方法では球形に近い形状の触媒担体がほぼ隙間なく充填されしかもホットプレスにより

互いに強固に密着して密度が高くなりガス流通路が十分に形成されず、ガス透過性が大きく損なわれている。燃料電池反応は燃料ガスが反応サイトに供給されなければ生じないため、触媒活性がいかに高くても燃料ガスが反応サイトに供給されなければ反応は生じない。従ってガス透過性は触媒活性より重要であるという見方も可能であり、ガス透過性の向上に対する考慮が殆どない従来の燃料電池はその触媒活性が十分に生かされていないとも言える。更に触媒層のうちイオン交換膜に近接する箇所ほど燃料電池反応への寄与が大きく触媒の利用率高く逆にガス拡散層に近接するほど触媒の利用率は低下するが、従来の触媒層が均一な燃料電池ではこの触媒利用率をより以上に向上させて最適値で燃料電池を運転するという考え方は存在しない。

【0006】

【発明が解決しようとする課題】そこで本発明は、触媒層の厚み方向にその機能、例えばイオン交換樹脂濃度、触媒濃度、触媒担体の緻密性及び触媒担体の比表面積等を変化させることにより燃料電池の触媒層のガス透過性とプロトン導伝性という相反した関係にある両機能をそれぞれ向上させた燃料電池を提供することを目的とする。

【0007】

【課題を解決するための手段】上記の課題を解決するための本発明は、触媒が担持された触媒担体とイオン交換樹脂、又は触媒が担持された触媒担体とイオン交換樹脂と親水性樹脂による触媒層が、イオン交換膜とガス拡散層間に形成された高分子固体電解質型燃料電池用電極において、前記触媒層の性能を該触媒層の厚さ方向に異ならせたことを特徴とする高分子固体電解質型燃料電池用電極である。前記性能としては、イオン交換樹脂濃度、触媒担体の比表面積あるいは緻密性及び触媒濃度等がある。なお該性能は触媒層のイオン交換膜側からガス拡散層側に均一勾配で変化する必要はなく、触媒層のイオン交換膜側の性能が全体としてガス拡散層側の性能と異なっていれば良い。

【0008】以下本発明を詳細に説明する。前述した通り燃料電池では、ガス拡散層側から燃料ガスを供給し該燃料ガスがガス拡散層を透過し更に触媒層を透過してイオン交換膜表面に達して反応が進行する。この反応はアノードでは水素ガスの酸化によるプロトン発生であり、カソードでは酸素ガスの還元による電子の発生である。アノード（カソード）で発生するプロトン（電子）は触媒層からガス拡散層を経て導線によりカソード（アノード）に接続された負荷を通ることにより初めて外部にエネルギーとして取り出される。従って触媒層の機能の1つであるプロトン（電子）導伝性から見ると、該機能を有するイオン交換樹脂が担持された触媒担体は緻密であることが望ましい。しかし触媒層の他の機能であるガス透過性の観点からは前記触媒担体は多孔質であることが

望ましい。

【0009】つまり触媒担体の緻密性に関して言えば、触媒層全体に亘って触媒担体の緻密性が均一であることは前述のガス透過性とプロトン（電子）導伝性の両者とともに向上させる観点からは望ましいことではない。従って本発明では、触媒担体の緻密性を触媒層の厚み方向に異ならせることにより、通常は二律背反の関係にある触媒層の主要性能であるガス透過性とプロトン（電子）導伝性をそれぞれ向上させることを可能にしている。つまり本発明では、燃料電池のイオン交換膜とガス拡散層間に配置された触媒層のイオン交換膜側に緻密な触媒担体をガス拡散層側に多孔質の触媒担体を配置し、前記緻密な触媒担体の触媒活性に優れた性能を反応サイトであるイオン交換膜近傍において十分に発揮させ、一方ガス拡散層側に多孔質の触媒担体を配置することにより、特に触媒層のガス拡散層側で要求されるガス透過性を向上させるようにしている。更に本発明では多孔質触媒担体を使用するため、該触媒担体がホットプレス等によっても完全に潰されることがなくガス流通路が確保され、過度のガス透過性の低下がない。好ましい触媒担体の緻密性例えば一次粒子径はイオン交換膜側が100～300 Å、ガス拡散層側が300 Å～1 μmである。

【0010】図2は、この触媒層の厚み方向で触媒担体の緻密性を異ならせた燃料電池の電極を示すものである。図の電極は、上側から順にイオン交換膜11、触媒層12及びガス拡散層13の順に積層され、触媒層12のうちイオン交換膜11側は緻密な触媒担体14により、又ガス拡散層13側は多孔質の触媒担体15により構成されている。この電極にはガス拡散層13の下方から水素や酸素の燃料ガスが供給され、イオン交換膜11からは生成するプロトン（電子）及び生成ガスが取り出される。ガス拡散層13側から供給される燃料ガスは該ガス拡散層13側の触媒担体15が多孔質であるためその間を容易に通過して両触媒担体14、15の界面まで達する。この界面からイオン交換膜11側の触媒担体14は緻密であるためガス透過能は低下するが、透過すべき距離が半分になっているため、全体としてはガス透過能が改善される。

【0011】一方イオン交換膜11近傍の反応サイトで生成するプロトン（電子）は導伝性を有するカーボン等の触媒担体を介して外部の導線に取り出されるが、触媒層12のイオン交換膜11側の触媒担体14が緻密でありつまり導伝体濃度が高いため、容易に前記両触媒担体14、15の界面まで達する。この界面からガス拡散層13側の触媒担体15は多孔質であるため導伝性は低下するが、導伝されるべき距離が半分になっているため、全体としては導伝性が改善される。更に前記反応サイトで生成するガスも前記触媒層12を通して取り出されるが、この場合にもガス拡散層13側の多孔質触媒担体15のため、全体のガス透過性が向上する。このような触媒層の厚み方向で異ならせる性質は触媒担体の多孔度に限定される訳ではなく、

その他に触媒担体の比表面積、イオン交換樹脂量及び触媒濃度等の性質を触媒層の厚み方向で異ならせても良い。

【0012】触媒担体の比表面積の触媒活性やガス透過性に対する影響は画一的には決定できないが、触媒担体の粒径が一定の場合に比表面積を増加させると、換言すると担体の細孔を増加させると、ガス流通路が増加してガス透過性が向上しかつ担体の連続性が損なわれるためプロトン（電子）導伝性は低下する。逆に触媒担体の粒径が一定の場合に比表面積を減少させると、換言すると担体の細孔を減少させるとガス流通路が減少してガス透過性が低下しかつ担体のプロトン（電子）導伝性が増加する。従ってイオン交換膜側の触媒担体の比表面積を小さくしガス拡散層側の触媒担体の比表面積を大きくすることにより、ガス透過性を高く維持しかつ反応活性も高い燃料電池を提供できる。好ましい触媒担体の比表面積はガス拡散層側が250～2000 $\text{m}^2/\text{g}$ であり、イオン交換樹脂側が50～400 $\text{m}^2/\text{g}$ である。次に触媒担体や撥水性樹脂（例えばポリテトラフルオロエチレンやフッ素化ポリエチレン-ポリプロピレン）とともに触媒層を構成するイオン交換樹脂は、プロトン（電子）の導伝性向上に寄与し、逆にガス透過性を低下させる。従って前記イオン交換樹脂濃度はイオン交換膜側で高くし、ガス拡散層側で低くすることにより、プロトン（電子）導伝性及びガス透過性の両者を高く維持できる。好ましいイオン交換樹脂濃度はガス拡散層側が20～50重量%、イオン交換樹脂側が40～70重量%である。

【0013】図3は、この触媒層の厚み方向でイオン交換膜量を異ならせた燃料電池の電極を示すものである。図の電極は、上側から順にイオン交換膜21、触媒層22及びガス拡散層23の順に積層され、触媒層22のうちイオン交換膜21側は担持されるイオン交換樹脂量が多い触媒担体24により、又ガス拡散層23側は担持されるイオン交換樹脂量が少ない触媒担体25により構成されている。この電極でも図2と同様にガス供給及びガス排出が行なわれ、ガス拡散層23側から供給される燃料ガスは該ガス拡散層23側の触媒担体25のイオン交換樹脂量が少ないため担体間を容易に通過して両触媒担体24、25の界面まで達する。この界面からイオン交換膜21側の触媒担体24はイオン交換樹脂量が多いためガス透過能は低下するが、透過すべき距離が半分になっているため、全体としてはガス透過能が改善される。又図2の場合と同様に、イオン交換膜21近傍の反応サイトで生成するプロトン（電子）及び生成ガスの取り出しも全体として改善される。

【0014】前述の触媒濃度を異ならせる場合も図3と同じように、イオン交換膜に近い側の触媒担体の触媒担持量を増加させ、ガス拡散層に近い側の触媒担体の触媒担持量を減少させて燃料電池用電極を構成する。好ましい触媒特に貴金属触媒の触媒担体に対する濃度はイオン交換膜側が30～60重量%、ガス拡散層側が10～40重量%

である。この場合にはガス透過性に関する改善は生じないが、反応サイトに近い触媒濃度が高いため触媒利用率が向上し、全体的な触媒活性が増加する。前述した厚み方向に性能を異ならせた触媒層は、例えばガス拡散層表面に、異なる混合比率（組成）又は原料を用いた懸濁液を複数回塗布もしくは2～10回塗布を繰り返すことにより、又は別個に調製した性能の異なる複数の触媒層前駆体を接合することにより得られる。一回の塗布で形成される薄膜の厚さは特に限定されないが5～20 $\mu\text{m}$ であることが好ましく、熱処理を行なう場合には、130～180 $^{\circ}\text{C}$ で10～30 $\text{kg}/\text{cm}^2$ の圧でホットプレスすれば良い。

#### 【0015】

【実施例】本発明の高分子固体電解質型燃料電池用電極の実施例を比較例とともに説明するが、これらは本発明を限定するものではない。

【実施例1】白金を1 $\text{mg}/\text{cm}^2$ 担持した（カーボン担体に対して30重量%）比表面積300 $\text{m}^2/\text{g}$ のカーボン担体を準備した。このカーボン担体3種を、それぞれ該カーボン担体に対する重量比が58.5%、50%及び38.5%であるイオン交換樹脂（ナフィオン、デュボン社の商品名）5%溶液の濃縮液20 $\text{g}$ と蒸留水6 $\text{g}$ とともに遊星ボールミルにて50分間混合してペーストを得た。イオン交換樹脂濃度が38.5%であるペーストを、30重量%の撥水性樹脂ポリテトラフルオロエチレンで撥水処理したカーボンペーパーから成るガス拡散層へ塗布し、60 $^{\circ}\text{C}$ で10分間乾燥し、更に130 $^{\circ}\text{C}$ 、20 $\text{kg}/\text{cm}^2$ で1分間焼成し、次にイオン交換樹脂濃度が50%であるペーストを同一条件で前記したペーパー上へ塗布しかつ焼成し、更にイオン交換樹脂濃度が58.5%であるペーストを同一条件で前記ペースト上へ塗布しかつ焼成して前記ガス拡散層上へ触媒層を形成して電極とした（電極面積 $\pi\text{cm}^2$ ）。

#### 【0016】

【実施例2】カーボン担体として粒径0.03 $\mu\text{m}$ 、表面積1300 $\text{m}^2/\text{g}$ のものを使用した。イオン交換樹脂のカーボン担体に対する重量比を50%とし、白金担持量が50重量%である実施例1と同じペーストを次いで白金担持量が40重量%である実施例1と同じペーストをガス拡散層へ塗布し、それぞれ60 $^{\circ}\text{C}$ で10分間乾燥し、更に130 $^{\circ}\text{C}$ 、20 $\text{kg}/\text{cm}^2$ で1分間焼成して触媒濃度が触媒層の厚み方向に異なる電極を製造した（電極面積 $\pi\text{cm}^2$ ）。

#### 【0017】

【比較例1】触媒層を、イオン交換樹脂の重量比がカーボン担体に対して50%である均一な触媒層としたこと以外は実施例1と同一条件でガス拡散層上へ触媒層を形成して電極とした。

【0018】上記のように製造された実施例1及び2の電極と比較例1の電極各2枚でイオン交換膜（デュボン社製ナフィオン112）を挟み、それぞれセル温度80 $^{\circ}\text{C}$ 、350 $\text{ml}/\text{分}$ で水素ガスを250 $\text{ml}/\text{分}$ で酸素ガスを供給しながら、電圧と電流密度の関係を測定したところ、図4

のグラフに示すような結果を得た。このグラフから、実施例1及び実施例2の電極は高電流密度領域で比較例1の電流よりも高電圧を得ることができ、特に実施例2（イオン交換樹脂濃度を異ならせた電極）の電極の方が実施例1（触媒濃度を異ならせた電極）よりも良好な効果が生じたことが判る。

#### 【0019】

【実施例3】ガス拡散層側の担体として白金を40重量%担持した（白金量は $0.5 \text{ mg/cm}^2$ ）比表面積が約 $1300 \text{ m}^2/\text{g}$ のカーボン担体を、又イオン交換膜側の担体として白金を40重量%担持した（白金量は $0.5 \text{ mg/cm}^2$ ）比表面積が約 $300 \text{ m}^2/\text{g}$ のカーボン担体をそれぞれ使用して、実施例1と同様にして電極を製造した（電極面積 $\pi \text{ cm}^2$ ）。

#### 【0020】

【比較例2】触媒層を、イオン交換樹脂の重量比がカーボン担体に対して50%であり、白金を30重量%担持した（白金量は $1 \text{ mg/cm}^2$ ）比表面積が約 $300 \text{ m}^2/\text{g}$ のカーボン担体を使用して構成し、均一な触媒層を有する電極を製造した（電極面積 $\pi \text{ cm}^2$ ）。

【0021】上記のように製造された実施例3と比較例2の電極各2枚でイオン交換膜（デュボン社製ナフィオン112）を挟み、それぞれセル温度 $80^\circ\text{C}$ 、 $350 \text{ ml}/\text{分}$ で水素ガスを $250 \text{ ml}/\text{分}$ で酸素ガスを供給しながら、電圧と電流密度の関係を測定したところ、図5のグラフに示すような結果を得た。このグラフから、実施例3の電極は高電流密度領域で比較例2の電流よりも高電圧を得ることができたことが判る。

#### 【0022】

【実施例4】ガス拡散層側の担体として、粒径 $0.03 \mu\text{m}$ 、表面積 $1300 \text{ m}^2/\text{g}$ のものを使用し、イオン交換膜側の担体として、粒径 $0.015 \mu\text{m}$ 、表面積 $1500 \text{ m}^2/\text{g}$ のものを使用し、白金を40重量%担持して（白金量は $1 \text{ mg/cm}^2$ ）電極面積が $\pi \text{ cm}^2$ である電極を製造した。この電極を使用して、上述の実施例1と同一条件で電圧と電流密度の関係を測定したところ、図6のグラフに示すような結果を得た。このグラフから、高電流密度領域でも比較的高電圧でエネルギーを取り出せたことが判る。

#### 【0023】

【発明の効果】本発明は、触媒が担持された触媒担体とイオン交換樹脂、又は触媒が担持された触媒担体とイオン交換樹脂と親水性樹脂による触媒層が、イオン交換膜とガス拡散層間に形成された高分子固体電解質型燃料電池用電極において、前記触媒層の性能を該触媒層の厚さ方向に異ならせたことを特徴とする高分子固体電解質型燃料電池用電極である（請求項1）。燃料電池の触媒層はガス透過性とプロトン（電子）導伝性という相反した性能を要求されるが、従来の燃料電池では比較的緻密な触媒担体やイオン交換樹脂をホットプレス等で結着して製造されている。この製法では球形に近い形状の触媒担体がほぼ隙間なく充填されしかもホットプレスにより互

いに強固に密着して密度が高くなりガス流通路は殆ど形成されず、ガス透過性が大きく損なわれている。

【0024】つまり従来の燃料電池では、燃料電池の触媒層の主たる機能であるガス透過性とプロトン等の導伝性のうち、ガス透過性を犠牲にしてプロトン等の導伝性を向上させることを意図している。しかしながら燃料ガスが反応サイトに供給され生成ガスが取り出されない限り反応は進行しない。従って従来の燃料電池では反応が十分速く進行せず、燃料電池の特性であるエネルギー生成が不十分となっている。この欠点を解消するために前記ホットプレスによる結着を弱くするとプロトン等の導伝性が損なわれ、ガスの供給及び排出は円滑に行なわれても、プロトン等の移動によるエネルギー生成が損なわれる。

【0025】前述の本発明では、触媒層の性能を該触媒層の厚さ方向に異ならせることにより、触媒層のイオン交換膜側とガス拡散層側でその主として達成される性能を相違させることにより、例えば前述のガス透過性及びプロトン等の導伝性に優れた燃料電池用電極を提供できる。この前記触媒層の厚み方向に異ならせる性能としては、第1にイオン交換樹脂濃度がある（請求項2）。イオン交換樹脂濃度が高いとプロトン等の導伝性は高くなるがガス透過性は低下する。従ってプロトン等の導伝性を必要とする触媒層のイオン交換膜側ではイオン交換樹脂濃度を高くし、プロトン等の導伝性をさほど必要とせず、むしろガス透過性を必要とする触媒層のガス透過性側ではイオン交換樹脂濃度を低くし、換言すると触媒層の厚み方向にイオン交換樹脂濃度の勾配を形成することにより、ガス透過性とプロトン等の導伝性に優れた燃料電池用電極を提供できる。

【0026】前述の触媒層の厚み方向に異ならせる性能としては、第2に触媒担体の比表面積がある（請求項3）。触媒担体の粒径が一定の場合に比表面積を増加させると、換言すると担体の細孔を増加させると、ガス流通路が増加してガス透過性が向上しかつ担体の連続性が損なわれるためプロトン等の導伝性は低下する。逆に触媒担体の粒径が一定の場合に比表面積を減少させると、換言すると担体の細孔を減少させるとガス流通路が減少してガス透過性が低下しかつ担体のプロトン等の導伝性が増加する。従って触媒層のイオン交換膜側の触媒担体の比表面積を小さくしガス拡散層側の触媒担体の比表面積を大きくすることにより、ガス透過性を高く維持しかつ反応活性も高い燃料電池を提供できる。

【0027】前述の触媒層の厚さ方向に異ならせる性能としては、第3に触媒担体の緻密性がある（請求項4）。触媒担体の緻密性が高いとプロトン等の導伝性は高くなる反面、ガス透過性は大きく減少する。従ってイオン交換膜側の触媒担体として緻密な触媒担体を、ガス透過性の触媒担体として多孔質の触媒担体を使用することにより、ガス透過性及びプロトン等の導伝性とも優れ



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**CLAIMS**


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[Claim(s)]

[Claim 1] The electrode for solid-polymer-electrolyte type fuel cells characterized by the catalyst bed containing the catalyst support with which the catalyst was supported, ion exchange resin or the catalyst support and ion exchange resin with which the catalyst was supported, and a water-repellent resin changing the performance of the aforementioned catalyst bed in the thickness direction of this catalyst bed in the electrode for solid-polymer-electrolyte type fuel cells formed between ion exchange membrane and the gaseous diffusion layer.

[Claim 2] The electrode for solid-polymer-electrolyte type fuel cells according to claim 1 which the aforementioned performance is ion-exchange-resin concentration, and uses high-concentration ion exchange resin and uses low-concentration ion exchange resin for the ion-exchange-membrane side of a catalyst bed at a gaseous diffusion layer side.

[Claim 3] The electrode for solid-polymer-electrolyte type fuel cells according to claim 1 which the aforementioned performance is the specific surface area of a catalyst support, uses a catalyst support with a small specific surface area for the ion-exchange-membrane side of a catalyst bed, and uses a catalyst support with a big specific surface area for a gaseous diffusion layer side.

[Claim 4] The electrode for solid-polymer-electrolyte type fuel cells according to claim 1 which the aforementioned performance is the compactness of a catalyst support, uses a precise catalyst support for an ion-exchange-membrane side, and uses a porous catalyst support for a gaseous diffusion layer side.

[Claim 5] The electrode for solid-polymer-electrolyte type fuel cells according to claim 1 which the aforementioned performance is the amount of catalysts, made [ many ] the amount of catalysts by the side of ion exchange membrane, and made small the amount of catalysts by the side of a gaseous diffusion layer.

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[Translation done.]

DERWENT-ACC-NO: 1997-518609

DERWENT-WEEK: 199748

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TITLE: Electrode for solid polymer electrolyte type fuel  
battery - has catalyst layer whose property is varied  
along its thickness direction

PATENT-ASSIGNEE: STONEHART ASSOC INC[STONN] ,  
TANAKA KIKINZOKU KOGYO  
KK[TANI], WATANABE M[WATAI]

PRIORITY-DATA: 1996JP-0082106 (March 11, 1996)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE
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JP 09245802 A	September 19, 1997	N/A 007
H01M 004/86		

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO
APPL-DATE		
JP 09245802A	N/A	1996JP-0082106
11, 1996		March

INT-CL (IPC): H01M004/86, H01M008/02 , H01M008/10

ABSTRACTED-PUB-NO: JP 09245802A

BASIC-ABSTRACT:

The electrode includes a catalyst layer (12) provided between an ion exchange membrane (11) and a gaseous diffusion layer (13). The catalyst layer includes catalyst support carrying catalyst ion exchange resin and the water repellent resin. The catalyst support comprises a dense catalyst support (14) by the side of ion exchange membrane and a porous catalyst support (15) by the side of gas diffusion layer. The property of catalyst layer is varied along its thickness direction.

ADVANTAGE - Proves high reaction activity. Does not impair conduction property and improves efficiency.

CHOSEN-DRAWING: Dwg.2/6

TITLE-TERMS: ELECTRODE SOLID POLYMER  
ELECTROLYTIC TYPE FUEL BATTERY CATALYST  
LAYER PROPERTIES VARY THICK DIRECTION

DERWENT-CLASS: A85 L03 X16

CPI-CODES: A12-E06A; A12-M; L03-E04B;

EPI-CODES: X16-C01C; X16-E06A;

## ENHANCED-POLYMER-INDEXING:

### Polymer Index [1.1]

018 ; P0000 ; K9621\*R

### Polymer Index [1.2]

018 ; ND01 ; K9745\*R ; Q9999 Q7341 Q7330 ; Q9999 Q7409  
Q7330 ; K9416  
; K9698 K9676 ; K9483\*R ; K9574 K9483

### Polymer Index [1.3]

018 ; Q9999 Q7772

### Polymer Index [2.1]

018 ; P0000

### Polymer Index [2.2]

018 ; ND01 ; K9745\*R ; Q9999 Q7341 Q7330 ; Q9999 Q7409  
Q7330 ; K9416  
; K9698 K9676 ; K9483\*R ; K9574 K9483

### Polymer Index [2.3]

018 ; B9999 B3509 B3485 B3372

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the aforementioned electrode for fuel cells which raised more the performance of the aforementioned catalyst bed in the electrode for fuel cells which changes from a catalyst bed and a gaseous diffusion layer to a detail about the electrode for solid-polymer-electrolyte type fuel cells.

[0002]

[The conventional technology and a trouble] Since a fuel cell is efficient and the pollution-free power plant which use hydrogen and various fossil fuels, it has a great hope socially as a power plant of "postatomic power" which can cope with energy problems and a full-terrestrial pollution problem. Various fuel cells according to the use, such as an object for steam-generated alternative power generation, an object for the on-site power generation of a building or a works unit, or an object for space, are developed. In recent years, the acid rain by the greenhouse effect centering on carbon dioxide gas, NO<sub>x</sub>, SO<sub>x</sub>, etc. is recognized as serious pollution which threatens the future of the earth. Since one of the main sources of ecocrisis of these pollution gas is internal combustion engines, such as an automobile, the tendency which uses a fuel cell as a motor power supply which replaces with the internal combustion engine for mount, and operates is increasing quickly. In this case, like many incidental facilities, the thing of a cell small as much as possible is desirable, and it is indispensable that for that the power density of the main part of a cell and output current density are high. The solid-polymer-electrolyte type fuel cell (it is called Following PEMFC) using ion exchange membrane as a candidate of a leading fuel cell who fulfills this condition attracts attention.

[0003] The basic structure of the main part of PEMFC, an operation, and a trouble are explained here. As shown in drawing 1, the foundations of a cell are constituted by joining the anode and cathode which are shown by 4A and 4C by the hotpress to the both sides of PEM1. This anode and cathode consist of gaseous diffusion layers, such as a carbon paper shown by the porous catalyst layer shown by 2A or 2C, 3A, or 3C. Electrode reaction occurs on the catalyst front face of 2A and 2C sections. Anode reactant gas (H<sub>2</sub>) is supplied through reactant gas feed-holes 5A to 3A, and cathode reactant gas (O<sub>2</sub>) is supplied through reactant gas feed-holes 5C to 3C. In 2A, it is anode-reaction:  $H_2 \rightarrow 2H^+ + 2e^-$ . - In 2C, it is a cathode reaction. : The reaction of  $1/2 O_2 + 2H^+ + 2e^- \rightarrow H_2 O$  occurs, and  $H_2 + 1/2 O_2 \rightarrow H_2 O + Q$  (heat of reaction) happens as these reactions being total by the whole cell. Electromotive force is obtained in this process, and electric work is made in case an electron flows the external load 8 with this electrical energy.

[0004] How the reaction of a fuel cell uses the aforementioned catalyst effectively by happening on the aforementioned catalyst or whether if it puts in another way, \*\*\*\* of a catalyst bed, as a result the performance of a fuel cell will be raised are the greatest factor which influences the amount of energy obtained by the aforementioned fuel cell. However, in the conventional fuel cell, the performance of a catalyst bed cannot be made into the maximum for various reasons, but there is a fault that the expensive catalyst,

especially the platinum metal catalyst cannot be used effectively. This invention persons found out that one of the reason of the was because the catalyst bed is uniform, as a result of considering carefully the reason which cannot make the performance of this fuel cell the maximum. From the former, the catalyst bed of the electrode for solid-polymer-electrolyte type fuel cells applies at once the suspension which ~~\*\*\*\*(ed) a catalyst, ion exchange resin or a catalyst and ion exchange resin~~, and the water-repellent resin into the mixed liquor of an organic solvent and water on an electrode substrate, it dries, and calcinates and is manufactured. In this method, since it applies at once, the hybrid raw material of a catalyst bed cannot be changed in the thickness direction of a catalyst bed, and the optimal catalyst bed according to each cannot be obtained in the thickness direction of a catalyst bed. The main functions of a catalyst bed are in the point which ~~\*\*\*\*~~ the proton and electron which are produced with an anode and a cathode, and promotes a fuel cell reaction. On the other hand, a catalyst bed supplies reactant gas and it also has the function to discharge generation gas, and greater importance comes to be attached than to the function to promote a reaction and to ~~\*\*\*\*~~ a proton to the function which makes gas-stream ~~\*\*~~ smooth, so that the same catalyst bed also separates from a reaction site. However, the conventional catalyst bed is uniform as above-mentioned, and its compactness of the catalyst support which gives the smooth nature of the gas-stream ~~\*\*~~ is also uniform.

[0005] It is impossible for the function, i.e., gas permeability which makes this gas-stream ~~\*\*~~ smooth, and proton (~~electron~~) conductivity to have an antinomy-relation, for another side to become low if one side is raised, and to raise both with the conventional technology. Ion exchange membrane of the conventional fuel cell is pinched by two electrodes (an anode and cathode) manufactured as mentioned above, and it binds these with a hotpress and is manufactured. The catalyst support of the configuration near a globular form is filled up with this method that there is almost no crevice, moreover, it sticks firmly mutually with a hotpress, density becomes high, and a gas-stream path is not fully formed, but gas permeability is spoiled greatly. A reaction is not produced if fuel gas will not be supplied to a reaction site however high catalytic activity may be, since a fuel cell reaction is not produced if fuel gas is not supplied to a reaction site. Therefore, the view that gas permeability is more important than catalytic activity is also possible, and the catalytic activity can say that it is not fully efficiently employed by the conventional fuel cell which does not almost have the consideration to the improvement in gas permeability. Furthermore, the view of raising this catalyst utilization factor above more in a fuel cell with the conventional uniform catalyst bed although the utilization factor of a catalyst falls so that the contribution to a fuel cell reaction is as large as the part which approaches ion exchange membrane among catalyst beds and the utilization factor of a catalyst approaches a gaseous diffusion layer highly and conversely, and operating a fuel cell with an optimum value does not exist.

[0006]

[Problem(s) to be Solved by the Invention] Then, this invention aims at offering the fuel cell which raised both the functions that have a conflicting relation called the gas permeability of the catalyst bed of a fuel cell, and proton conductivity, respectively by changing the compactness of the function, for example, ion-exchange-resin concentration, catalyst concentration, and a catalyst support, the specific surface area of a catalyst support, etc. in the thickness direction of a catalyst bed.

[0007]

[Means for Solving the Problem] this invention for solving the above-mentioned technical problem is an electrode for solid-polymer-electrolyte type fuel cells to which the catalyst bed by the catalyst support with which the catalyst was supported, ion exchange resin, or the catalyst support, the ion exchange resin and the water-repellent resin with which the catalyst was supported is characterized by changing the performance of the aforementioned catalyst bed in the thickness direction of this catalyst bed in the electrode for solid-polymer-electrolyte type fuel cells formed between ion exchange membrane and the gaseous diffusion layer. As the aforementioned performance, there are specific surface area or compactness, catalyst concentration, etc. of ion-exchange-resin concentration and a catalyst support. In addition, this performance does not need to change from the ion-exchange-membrane side of a catalyst bed to a gaseous diffusion layer side with uniform

inclination, and the performance by the side of the ion exchange membrane of a catalyst bed should just differ from the performance by the side of a gaseous diffusion layer as a whole.

[0008] this invention is explained in detail below. In a fuel cell, fuel gas is supplied from a gaseous diffusion layer side, this fuel gas penetrates a gaseous diffusion layer, a catalyst bed is penetrated further, an ion-exchange-membrane front face is arrived at, and a reaction advances as mentioned above. This reaction is proton generating by oxidization of hydrogen gas in an anode, and is generating of the electron by reduction of oxygen gas in a cathode. The proton (electron) generated with an anode (cathode) is taken out as energy outside for the first time by passing along the load connected to the cathode (anode) by lead wire through the gaseous diffusion layer from the catalyst bed. Therefore, when it sees from the proton (electron) conductivity which is one of the functions of a catalyst bed, the catalyst support with which the ion exchange resin which has this function was supported has a precise desirable thing. However, as for the aforementioned catalyst support, from a viewpoint of gas permeability which are other functions of a catalyst bed, it is desirable that it is porosity.

[0009] That is, if it says about the compactness of a catalyst support, from a viewpoint which covers the whole catalyst bed and raises both gas permeability of the above-mentioned [ that the compactness of a catalyst support is uniform ], and both proton (electron) conductivity, it will not be desirable. Therefore, in this invention, it makes it possible to raise the gas permeability which is the main performance of the catalyst bed which usually has an antinomy-relation, and proton (electron) conductivity, respectively by changing the compactness of a catalyst support in the thickness direction of a catalyst bed. That is, in this invention, a porous catalyst support is arranged for a catalyst support precise to the ion-exchange-membrane [ of a fuel cell ], and ion-exchange-membrane side of the catalyst bed arranged between gaseous diffusion layers to a gaseous diffusion layer side. the above -- fully demonstrating the performance excellent in the catalytic activity of a precise catalyst support [ near / which is a reaction site / the ion exchange membrane ], and arranging a porous catalyst support to a gaseous diffusion layer side on the other hand -- especially, it is made to raise the gas permeability demanded by the gaseous diffusion layer side of a catalyst bed Furthermore, in order to use porous catalyst support in this invention, this catalyst support is not completely crushed by the hotpress etc., a gas-stream path is secured, and too much fall of gas permeability cannot be found. An ion-exchange-membrane side is [ a 100 - 300 \*\* and gaseous diffusion layer side ] 300 \*\*-1micrometer, the compactness of a primary particle, for example, the diameter, of a desirable catalyst support.

[0010] Drawing 2 shows the electrode of the fuel cell which changed the compactness of a catalyst support in the thickness direction of this catalyst bed. The laminating of the electrode of drawing is carried out to order from the bottom at the order of ion exchange membrane 11, a catalyst bed 12, and the gaseous diffusion layer 13, and the gaseous diffusion layer 13 side is constituted by the porous catalyst support 15 among catalyst beds 12 by the catalyst support 14 with a precise ion-exchange-membrane 11 side again. The fuel gas of hydrogen or oxygen is supplied to this electrode from the lower part of the gaseous diffusion layer 13, and the proton (electron) and generation gas to generate are taken out from ion exchange membrane 11. Since the catalyst support 15 by the side of this gaseous diffusion layer 13 is porosity, the fuel gas supplied from the gaseous diffusion layer 13 side passes the meantime easily, and attains it to the interface of both the catalyst supports 14 and 15. Although gas penetrability falls from this interface since the catalyst support 14 by the side of ion exchange membrane 11 is precise, since the distance which should be penetrated is half, gas penetrability is improved as the whole.

[0011] Although taken out by external lead wire through catalyst supports, such as carbon which has conductivity, since [ that the catalyst support 14 by the side of the ion exchange membrane 11 of a catalyst bed 12 is precise that is, ] \*\*\*\*\* concentration is high, the proton (electron) generated to an about 11 ion exchange membrane reaction site on the other hand is easily attained to the interface of both the aforementioned catalyst supports 14 and 15. Although conductivity falls from this interface since the catalyst support 15 by the side of the gaseous diffusion layer 13 is porosity, since the distance which should be \*\*\*\*

(ed) is half, conductivity is improved as the whole. Furthermore, although the gas generated to the aforementioned reaction site is also taken out through the aforementioned catalyst bed 12, the whole gas permeability improves also in this case for the porous catalyst support 15 by the side of the gaseous diffusion layer 13. The property changed in the thickness direction of such a catalyst bed is not necessarily limited to the porosity of a catalyst support, in addition may change properties, such as specific surface area of a catalyst support, the amount of ion exchange resin, and catalyst concentration, in the thickness direction of a catalyst bed.

[0012] Although the influence to the catalytic activity of the specific surface area of a catalyst support or gas permeability cannot be determined uniformly, if the pore of support is made to increase when it will put in another way, if specific surface area is made to increase when the particle size of a catalyst support is fixed, since a gas-stream path will increase, and gas permeability will improve and the continuity of support will be spoiled, proton (electron) conductivity falls. Conversely, if specific surface area is decreased when the particle size of a catalyst support is fixed, it will put in another way and the pore of support will be decreased, gas-stream paths will decrease in number, and gas permeability will fall, and the proton (electron) conductivity of support will increase. Therefore, by making small specific surface area of the catalyst support by the side of ion exchange membrane, and enlarging specific surface area of the catalyst support by the side of a gaseous diffusion layer, gas permeability is maintained highly and a fuel cell also with high reaction activity can be offered. A gaseous diffusion layer side is 250-2000m<sup>2</sup>/g, and the ion-exchange-resin side of the specific surface area of a desirable catalyst support is 50-400 m<sup>2</sup>/g. Next, the ion exchange resin which constitutes a catalyst bed with a catalyst support or a water-repellent resin (for example, a polytetrafluoroethylene and fluoridation polyethylene-polypropylene) contributes to the improvement in conductive of a proton (electron), and reduces gas permeability conversely. Therefore, the aforementioned ion-exchange-resin concentration can maintain highly both proton (electron) conductivity and gas permeability by making it high and making it low by the gaseous diffusion layer side by the ion-exchange-membrane side. A gaseous diffusion layer side is [ the ion-exchange-resin side of desirable ion-exchange-resin concentration ] 40 - 70 % of the weight 20 to 50% of the weight.

[0013] Drawing 3 shows the electrode of the fuel cell which changed the amount of ion exchange membrane in the thickness direction of this catalyst bed. The laminating of the electrode of drawing is carried out to order from the bottom at the order of ion exchange membrane 21, a catalyst bed 22, and the gaseous diffusion layer 23, and the gaseous diffusion layer 23 side is constituted by the catalyst support 24 with many amounts of ion exchange resin with which an ion-exchange-membrane 21 side is supported among catalyst beds 22 again by the catalyst support 25 with few amounts of ion exchange resin supported. Gas supply and gas ejection are performed by this electrode as well as drawing 2, and since the fuel gas supplied from the gaseous diffusion layer 23 side has few amounts of ion exchange resin of the catalyst support 25 by the side of this gaseous diffusion layer 23, it passes through between support easily and attains it to the interface of both the catalyst supports 24 and 25. Although gas penetrability falls from this interface since the catalyst support 24 by the side of ion exchange membrane 21 has many amounts of ion exchange resin, since the distance which should be penetrated is half, gas penetrability is improved as the whole. Moreover, the ejection of the proton (electron) generated to an about 21 ion exchange membrane reaction site and generation gas as well as the case of drawing 2 is improved as a whole.

[0014] As well as drawing 3 when it changes the above-mentioned catalyst concentration, the amount of catalyst support of the catalyst support of the side near ion exchange membrane is made to increase, the amount of catalyst support of the catalyst support of the side near a gaseous diffusion layer is decreased, and the electrode for fuel cells is constituted. An ion-exchange-membrane side is [ the gaseous diffusion layer side of the concentration to the catalyst support of a desirable catalyst, especially a noble metal catalyst ] 10 - 40 % of the weight 30 to 60% of the weight. In this case, although the improvement about gas permeability is not produced, since the catalyst concentration near a reaction site is high, a catalyst utilization factor improves,



and overall catalytic activity increases. the mixing ratio from which the catalyst bed which changed the performance in the thickness direction mentioned above differs for example, on a gaseous diffusion layer front face -- the suspension using the rate (composition) or the raw material -- multiple times -- repeating an application 2 to 10 times desirably -- or it is obtained by joining two or more catalyst bed precursors with which the performances prepared separately differ What is necessary is it to be desirable that it is 5-20 micrometers although especially the thickness of the thin film formed by one application is not limited, and just to carry out the hotpress of it by \*\* of 10 - 30 kg/cm<sup>2</sup> by 130 - 180 \*\*, in heat-treating.

[0015]

[Example] Although the example of the electrode for solid-polymer-electrolyte type fuel cells of this invention is explained with the example of comparison, these do not limit this invention.

[Example 1] The carbon support of specific-surface-area (it is 30 % of the weight to carbon support) 300 m<sup>2</sup>/g which supported platinum two times 1 mg/cm was prepared. Three sorts of these carbon support was mixed for 50 minutes with the planet ball mill with 20g of concentration liquid and 6g of distilled water of 5% (tradename of Nafion and Du Pont) solution of ion exchange resin whose weight ratios to this carbon support are 58.5%, 50%, and 38.5%, respectively, and the paste was obtained. It applies to the gaseous diffusion layer which consists of the carbon paper which carried out water-repellent treatment of the paste whose ion-exchange-resin-concentration is 38.5% by 30% of the weight of the water-repellent resin polytetrafluoroethylene. Dry for 10 minutes at 60 degrees C, and also it calcinates for 1 minute by 130 \*\* and 20 kg/cm<sup>2</sup>. Next, apply the paste whose ion-exchange-resin concentration is 50% to up to the paper described above on the same conditions, and it is calcinated. Furthermore, on the same conditions, ion-exchange-resin concentration applied to up to the aforementioned paste the paste which is 58.5%, and calcinated it, formed the catalyst bed in up to the aforementioned gaseous diffusion layer, and considered as the electrode (electrode area picm<sup>2</sup>).

[0016]

[Example 2] The thing of the particle size of 0.03 micrometers and surface-area of 1300m<sup>2</sup>/g was used as carbon support. The electrode from which the weight ratio to the carbon support of ion exchange resin is made into 50%, the same paste as the example 1 whose amount of platinum support is 50 % of the weight, and the example 1 whose amount of platinum support is subsequently 40 % of the weight about the same paste is applied to a gaseous diffusion layer, and it dries for 10 minutes at 60 degrees C, respectively, and also it calcinates for 1 minute by 130 \*\* and 20 kg/cm<sup>2</sup>, and catalyst concentration differs in the thickness direction of a catalyst bed be manufactured (electrode

[0017]

[The example 1 of comparison] Except the weight ratio of ion exchange resin having made the catalyst bed the uniform catalyst bed which is 50% to carbon support, the catalyst bed was formed in up to a gaseous diffusion layer on the same conditions as an example 1, and it considered as the electrode.

[0018] When the relation between voltage and current density was measured having supplied hydrogen gas by part for cell temperature [ of 80 degrees C ], and 350ml/, and supplying [ pinched ion exchange membrane (Du Pont Nafion 112) by the electrode of examples 1 and 2 and two electrodes each of the example 1 of comparison which were manufactured as mentioned above, ] oxygen gas by part for 250 ml/, respectively, the result as shown in the graph of drawing 4 was obtained. This graph shows that the electrode of an example 1 and an example 2 could obtain the high voltage rather than the current of the example 1 of comparison in the high current density field, and the effect with the electrode of an example 2 (electrode which changed ion-exchange-resin concentration) especially better than an example 1 (electrode which changed catalyst concentration) arose.

[0019]

[Example 3] The carbon support whose specific surface area (the amount of platinum is 0.5 mg/cm<sup>2</sup>) which supported platinum 40% of the weight as support by the side of a gaseous diffusion layer is about 1300m<sup>2</sup>/g

Moreover, the carbon support whose specific surface area (the amount of platinum is 0.5 mg/cm<sup>2</sup>) which supported platinum 40% of the weight as support by the side of ion exchange membrane is abbreviation 300 m<sup>2</sup>/g was used, respectively, and the electrode was manufactured like the example 1 (electrode area picm<sup>2</sup>). [0020]

[The example 2 of comparison] About a catalyst bed, the weight ratio of ion exchange resin is 50% to carbon support, the specific surface area (the amount of platinum is 1 mg/cm<sup>2</sup>) which supported platinum 30% of the weight constituted using the carbon support which is abbreviation 300 m<sup>2</sup>/g, and the electrode which has a uniform catalyst bed was manufactured (electrode area picm<sup>2</sup>).

[0021] When the relation between voltage and current density was measured having supplied hydrogen gas by part for cell temperature [ of 80 degrees C ], and 350 ml/, and supplying [ pinched each ion exchange membrane (Du Pont Nafion 112) by two electrodes of the example 3 manufactured as mentioned above and the example 2 of comparison ] oxygen gas by part for 250 ml/, respectively, the result as shown in the graph of drawing 5 was obtained. This graph shows that the electrode of an example 3 was able to obtain the high voltage rather than the current of the example 2 of comparison in the high current density field.

[0022]

[Example 4] as the support by the side of a gaseous diffusion layer -- the thing of the particle size of 0.03 micrometers, and surface-area of 1300m<sup>2</sup>/g -- using it -- as the support by the side of ion exchange membrane -- particle size 0.015 the thing of mum and surface-area of 1500m<sup>2</sup>/g -- using it -- platinum -- 40 % of the weight -- supporting -- electrode (amount of platinum is 1 mg/cm<sup>2</sup>) area -- picm<sup>2</sup> it is -- the electrode was manufactured When this electrode was used and the relation between voltage and current density was measured on the same conditions as the above-mentioned example 1, the result as shown in the graph of drawing 6 was obtained. This graph shows that energy was able to be comparatively taken out by the high voltage also in the high current density field.

[0023]

[Effect of the Invention] It is the electrode for solid-polymer-electrolyte type fuel cells characterized by this invention changing the performance of the aforementioned catalyst bed in the thickness direction of this catalyst bed in the electrode for solid-polymer-electrolyte type fuel cells by which the catalyst bed by the catalyst support with which the catalyst was supported, ion exchange resin, or the catalyst support, the ion exchange resin and the water-repellent resin with which the catalyst was supported was formed between ion exchange membrane and the gaseous diffusion layer (claim 1). Although the conflicting performance of gas permeability and proton (electron) conductivity is required of the catalyst bed of a fuel cell, by the conventional fuel cell, comparatively precise catalyst support and ion exchange resin are bound with a hotpress etc., and it is manufactured. The catalyst support of the configuration near a globular form is filled up with this process that there is almost no crevice, moreover, it sticks firmly mutually with a hotpress, and density becomes high, most gas-stream paths are not formed but gas permeability is spoiled greatly.

[0024] That is, in the conventional fuel cell, it has the intention of raising conductivity, such as a proton, at the sacrifice of gas permeability among the gas permeability which is the main function of the catalyst bed of a fuel cell, and conductivity, such as a proton. However, unless fuel gas is supplied to a reaction site and generation gas is taken out, a reaction does not advance. Therefore, a reaction does not advance sufficiently quickly but the conventional fuel cell of the energy generation which is the property of a fuel cell is inadequate. If binding by the aforementioned hotpress is weakened in order to cancel this fault, even if conductivity, such as a proton, will be spoiled and supply and ecrisis of gas will be performed smoothly, the energy generation by movement of a proton etc. is spoiled.

[0025] In the above-mentioned this invention, the electrode for fuel cells excellent in conductivity, such as the above-mentioned gas permeability and a proton, can be offered by making the performance mainly attained different by the ion-exchange-membrane [ of a catalyst bed ], and gaseous diffusion layer side by changing the performance of a catalyst bed in the thickness direction of this catalyst bed. As a performance which

makes it differ in the thickness direction of this aforementioned catalyst bed, ion-exchange-resin concentration is in the 1st (claim 2). If ion-exchange-resin concentration is high, although conductivity, such as a proton, will become high, gas permeability falls. Therefore, at the ion-exchange-membrane side of the catalyst bed which needs conductivity, such as a proton, by the gas permeability side of the catalyst bed which makes ion-exchange-resin concentration high, and does not need conductivity, such as a proton, so much, but needs gas permeability rather, if ion-exchange-resin concentration is made low and put in another way, the electrode for fuel cells excellent in gas permeability and conductivity, such as a proton, can be offered by forming the inclination of ion-exchange-resin concentration in the thickness direction of a catalyst bed.

[0026] There is [ 2nd ] specific surface area of a catalyst support as a performance which makes it differ in the thickness direction of the above-mentioned catalyst bed (claim 3). If the pore of support is made to increase when it will put in another way, if specific surface area is made to increase when the particle size of a catalyst support is fixed, since a gas-stream path will increase, and gas permeability will improve and the continuity of support will be spoiled, conductivity, such as a proton, falls. Conversely, if specific surface area is decreased when the particle size of a catalyst support is fixed, it will put in another way and the pore of support will be decreased, gas-stream paths will decrease in number, and gas permeability will fall, and conductivity, such as a proton of support, will increase. Therefore, by making small specific surface area of the catalyst support by the side of the ion exchange membrane of a catalyst bed, and enlarging specific surface area of the catalyst support by the side of a gaseous diffusion layer, gas permeability is maintained highly and a fuel cell also with high reaction activity can be offered.

[0027] There is [ 3rd ] compactness of a catalyst support as a performance which makes it differ in the thickness direction of the above-mentioned catalyst bed (claim 4). If the compactness of a catalyst support is high, while conductivity, such as a proton, will become high, gas permeability decreases greatly. Therefore, the electrode for fuel cells which was excellent also with conductivity, such as gas permeability and a proton, by using a porous catalyst support as a catalyst support of gas permeability in the catalyst support precise as a catalyst support by the side of ion exchange membrane can be offered. There is the amount of catalysts (concentration) as a performance of the last which makes it differ in the thickness direction of the above-mentioned catalyst bed (claim 5). Even if the reaction of a fuel cell decreases the catalyst concentration by the side of a gaseous diffusion layer, making high catalyst concentration by the side of ion exchange membrane among catalyst beds since it mainly happens by the ion-exchange-membrane side of a catalyst bed, it can reduce the expensive amount of catalysts which substantial catalytic activity does not fall and is used.

た燃料電池用電極を提供できる。前述の触媒層の厚さ方向に異ならせる最後の性能として触媒量（濃度）がある（請求項5）。燃料電池の反応は触媒層のイオン交換膜側で主として起こるため、触媒層のうちイオン交換膜側の触媒濃度を高くしたままガス拡散層側の触媒濃度を減少させても実質的な触媒活性が低下することがなく、使用する高価な触媒量を低減させることができる。

【図面の簡単な説明】

【図1】従来のイオン交換膜を使用した燃料電池の基本構造を示す概略図。

【図2】本発明の高分子固体電解質型燃料電池用電極の一実施例を示す断面図。

【図3】本発明の高分子固体電解質型燃料電池用電極の

他の実施例を示す断面図。

【図4】実施例1、2及び比較例1における電流密度と電圧の関係を示すグラフ。

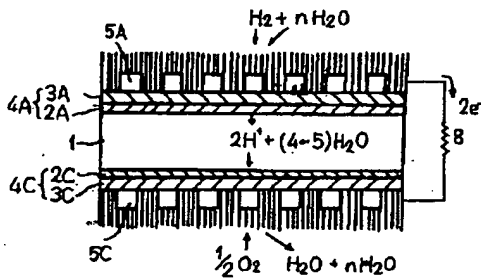
【図5】実施例3及び比較例2における電流密度と電圧の関係を示すグラフ。

【図6】実施例4における電流密度と電圧の関係を示すグラフ。

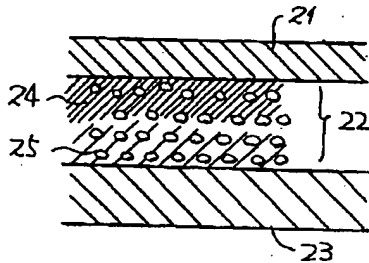
【符号の説明】

- 11、21、・・・イオン交換膜 12、22・・・触媒層 1  
3、23・・・ガス拡散層  
14、24・・・イオン交換膜側触媒担体 15、25・・・ガス拡散層側触媒担体

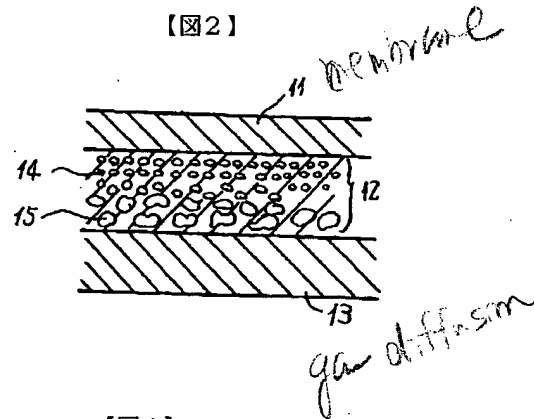
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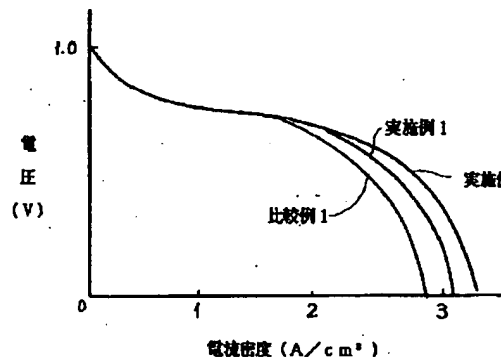
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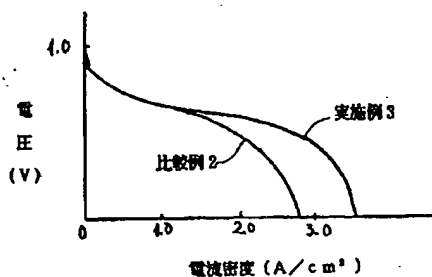
【図2】



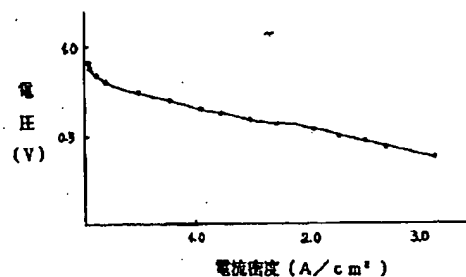
【図4】



【図5】



【図6】



## フロントページの続き

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